

Draft Conceptual Site Model Criteria Support Document for the Dewey-Burdock Project

1. Introduction

1.1. Project Site Description and History

The Dewey-Burdock Project is located on the edge of the Black Hills Uplift, in the southwestern corner of South Dakota. The structure of the project area is marked by sediments dipping gently to the southwest, with no major faults (Powertech, 2013). The units of primary interest for the proposed mining activities include the Inyan Kara Group, the Graneros Group, and the Morrison Formation. The uranium ore is hosted in the Inyan Kara Group, specifically within the sandstones of the Chilson Member of the Lakota Formation, and the Fall River Formation. In the project area, the two are separated by the Fuson Shale. Overlying the Inyan Kara is the Graneros Group, a sequence of marine shales that provide upper confinement of the ore zone. Beneath the Inyan Kara is the Jurassic-age Morrison Formation, a low-permeability shale that confines the ore zone from the older sediments below (Powertech, 2013).

Unlike coal or metal ores, which are mined by physical means, the uranium ore in the Inyan Kara consists of small, trace minerals that are diffuse throughout the rock. To extract them, Powertech is proposing to use in-situ recovery, or ISR (Powertech, 2013). The ISR process involves injecting the ore zone with a chemical solution, or lixiviant, which flows through the ore zone, dissolving the uranium. The lixiviant is then pumped to the surface and the uranium is extracted from solution (IAEA, 2016). For the Dewey-Burdock project, the lixiviant will be groundwater fortified with oxygen, which will dissolve the uranium, and carbon dioxide, which will bond with the dissolved uranium to keep it in solution. The uranium will be removed from the solution by ion exchange and will be processed into yellowcake. The fluid will then be refortified and recirculated through the ore zone (Powertech, 2013).

Uranium mineralization in the Dewey-Burdock area has been known to researchers since its discovery in 1951. Early investigations in the southern Black Hills were undertaken by the U.S. Geological Survey (USGS) in the 1950s and early 60s (Schnabel, 1963). Further work on the region's stratigraphy and roll-front uranium deposits was conducted by the USGS in 1974 and by the Tennessee Valley Authority in 1980 (Gott et al. 1974; Boggs and Jenkins, 1980). In 1990 the USGS launched the Black Hills Hydrology Study, which ran until 2002 and produced extensive data about the major aquifers in the area, including the Inyan Kara (Driscoll et al. 2002). Since then, more work has been done on gathering geochemical data and developing models of the Dewey-Burdock site. The USGS has carried out several studies on reactive transport modeling of the project area (Johnson, 2011; Johnson and Tutu, 2013; and Johnson et al. 2016a), and Powertech has also conducted groundwater numerical flow modeling (Petrotek, 2012). Since the discovery of the ore, thousands of exploration holes have been drilled at the Dewey-Burdock site (Powertech, 2013).

Although the geology, hydrology, and uranium mineralization of the Dewey-Burdock project area have been studied for decades, there are still gaps in the available data. The size and complexity of the project site also underscore the need for robust site characterization in order to fully assess the

potential impacts of ISR activities on groundwater resources. For example, previous site modeling has resulted in sorption process predictions with high uncertainty (Johnson and Tutu, 2013). More data are needed, particularly solid-phase core data, and sampling has not been conducted throughout the project site (Johnson et al. 2013). Synthesis of available geologic, hydrogeologic, and geochemical data and collection of additional data where needed will lead to an improved ability to simulate the mobilization and transport of contaminants at the site.

1.2. Purpose of Support Document

The purpose of this conceptual site model (CSM) support document is to describe the site-specific geologic, hydrogeologic, and geochemical site characteristics and processes that will support the development of a CSM for the Dewey-Burdock site. This document provides description and context for an accompanying document detailing criteria for development of a CSM for the Dewey-Burdock site.

A CSM based on a sufficient data set (i.e., types and amount of data) will support the development of a robust geochemical model for predicting fluid movement and groundwater quality changes throughout the project life cycle. Modeling based on a well-developed CSM will also improve the potential for detection of excursions of uranium or other metals beyond the aquifer exemption area and rebounding of uranium concentrations after site restoration.

Understanding the **geologic characteristics** (e.g., depth, thickness, lithology/mineralogy, and stratigraphy) of the injection interval, the upper and lower confining zones, and all underground sources of drinking water (USDWs) that may be affected by ISR-related activities will support the development of a CSM that accurately represents the geologic factors that influence groundwater flow and geochemical processes, including between the injectate (lixiviant), native groundwater, and the rock matrix (aquifer solids). See Section 2.

A detailed understanding of site **hydrogeologic characteristics** (e.g., permeability, porosity, pressure, transmissivity, storativity) will support simulation of the movement of injected and native fluids throughout the project's lifecycle. Baseline data feed the CSM and inform initial conditions; changes to these characteristics collected via site monitoring throughout site operations can be used to verify the modeled predictions and update the model as needed. See Section 3.

Characterization of the **geochemistry of the native fluids and solids within the injection formation** and incorporation of that information into the CSM is crucial for development and validation of a robust geochemical model to simulate geochemical changes (i.e., uranium speciation and mobilization) as ISR proceeds, restoration is performed, and the system eventually stabilizes after restoration. See Section 4.

Ideally, the data set on which the CSM is based will:

- Include information about the injection interval, the upper and lower confining zones, and all USDWs that may be affected by ISR-related activities;
- Be based on historic data and additional baseline data collection and updated with monitoring data during the course of the project;
- Represent the entire project, including upgradient and potentially affected downgradient areas;
- Be as detailed as possible to reflect any localized variability/heterogeneity;

- Reflect baseline conditions and the entire lifecycle of the project (i.e., ISR, restoration, and post-restoration); and
- Explain any data gaps and their potential impact on the certainty of the modeling results.

1.3. Geology of Uranium Roll-Front Deposits and In-Situ Recovery

The Dewey-Burdock project will be using in-situ recovery, a somewhat less common mining technique, to extract uranium from a roll-front type ore deposit. Uranium is not an abundant element in the Earth's crust and therefore must be concentrated by geologic processes before it can be mined in economic amounts. At Dewey-Burdock, as at the locations of 25% of the world's uranium resources, the uranium has been concentrated in what is known as a roll-front deposit (Saunders et al., 2016). Understanding the formation of roll-front uranium deposits and the process by which they are mined is crucial for the development of the CSM because their unique chemical and physical properties control the potential movement of uranium and other metals both during and after recovery.

Roll-front uranium deposits form in sandstone formations and are epigenetic, meaning that the ore is formed after the host sandstone has been deposited. A typical roll-front deposit is formed by the flow of groundwater containing uranium through the sandstone. Uranium is soluble in water in its oxidized state, U(VI). In most cases, the groundwater initially leaches the uranium from a source rock such as a granite or volcanic tuff (Saunders et al., 2016). As the uranium-enriched groundwater flows through the host sandstone, the uranium precipitates out of solution when it encounters reducing conditions (i.e., meets a reduction/oxidation or redox front). This means that the uranium is changed from the U(VI) state to U(IV), which is significantly less soluble in water. These reducing conditions are caused by the presence of reducing agents such as organic material (plant debris, marine algae, etc.), sulfide minerals, hydrocarbons, or interbedded volcanic rocks (Saunders et al., 2016). Because the uranium precipitates out of solution as the water flows through reducing regions in the sandstone, the resulting uranium deposits form in a lens shape pointing in the direction of groundwater flow. The uranium crystallizes in secondary minerals such as uraninite, pitchblende, or coffinite (Saunders et al., 2016). Roll-front deposits can also contain a suite of other secondary minerals depending on the original groundwater composition (see [REF _Ref7854310 \h] in Section 4.2). Finally, as oxygenated groundwater continues to flow through the sandstone, the previously immobilized uranium can dissolve again, be carried a short distance, and reprecipitate at the moving redox front. Hence the name "roll-front," because these uranium deposits can "roll" forward through the host sandstone in waves of mineralization.

The process of in-situ recovery (ISR) mimics the deposition of roll-front deposits but in reverse. A chemical mining solution, or lixiviant, is pumped through the host sandstone. This solution oxidizes the uranium and leaches it out of the rock. In the case of Dewey-Burdock, it will contain dissolved oxygen, to oxidize the uranium, and carbon dioxide, a complexing agent that will bind with the newly-dissolved uranium and prevent it from reprecipitating as the solution flows through the rock (Powertech, 2013). After flowing through the ore zone, the lixiviant is pumped from extraction wells, and the uranium is removed from the lixiviant via ion exchange. The design of the well field can vary depending on the shape and distribution of the deposit. Injection and extraction wells may be placed in alternating rows across the field, or in closely-spaced "spot" patterns, in which an injection well is surrounded by extraction wells in a 30 to 60-meter diameter circle (World Nuclear Association, 2009). ISR activities pose unique environmental risks because they involve mobilizing radioactive materials and heavy metals

in the Earth. Post-ISR restoration is dependent on the site-specific hydrology, geology, and geochemistry. Therefore, building an accurate CSM is important. Remediation of the site can include injecting reagents to restore original acidity/alkalinity, washing or flushing the formation zone with uncontaminated groundwater, or cleaning mining fluids either above ground or in-situ, among other possible restoration techniques (IAEA, 2016). Understanding the unique characteristics of the project site is crucial for designing an ISR remediation plan that adequately mitigates the risk of environmental damage.

2. Background and Considerations for Geologic Criteria

Because the computational simulations that this CSM will support are only an approximation of an actual system, using as complete a geologic data set as possible will support accurate predictions of system behavior. Therefore, the CSM and subsequent reactive transport model should incorporate information about the injection interval, the upper and lower confining zones, and all USDWs that may be affected by ISR-related activities at the Dewey-Burdock site. This information may be based on historic data, with areas where data are lacking “filled in” by additional baseline data collection. Data should be collected according to accepted industry methods with supporting documentation of quality and reliability. Information about formation depth, thicknesses, and lithologic, petrologic and mineralogic characteristics supports a realistic representation of the geology of the project site in the CSM and in the reactive transport model domain. Information about the lithologic characteristics will dovetail with geochemical data on the solids to support predictions of the interactions between the fluids and the aquifer solids. Additionally, the overall geologic structure should be described because larger-scale features may affect fluid movement/confinement.

Geologic data may be based on historical information about the site or site-specific data gathering. It should (1) cover the entire project area with an adequate margin so that all features that may affect fluid flow are represented, and (2) be as detailed as possible to reflect information on lithologic variability within the project area that could impact fluid movement at a localized scale. Any data gaps (either due to natural heterogeneity or missing data) and their potential impact on the modeling results should be identified so that the modeling results (and their certainty) can be evaluated in the appropriate context. For example, if data in an area are sparse, but the formation is generally homogeneous, this may be less of a concern than data gaps in an area where the formation is more heterogeneous.

A full geologic characterization of the Dewey-Burdock site will include descriptions of both the Inyan Kara Group and the major confining layers: the Graneros Group and the Morrison Formation. The areal extent, continuity, and boundaries of each member of the Inyan Kara Group will need to be described, as well as the locations of the ore bodies they contain. Their depths, structures, and thicknesses must be described, as well as any information on hydraulic connections between the sandstone members and the continuity of localized confining layers. Their lithology and depositional histories are important for assessing their permeability and the potential for preferential flowpaths of fluids through sediment channels. Other petrologic and mineralogic characteristics, such as grain size, cementation, overgrowths, and nodules can all affect fluid flow through the rock, and should therefore be documented and included in the CSM.

The operational confining zones will need to be similarly described, including their areal extent and continuity, the presence of any faults and fractures that would reduce their integrity, and their depth and structure. The thicknesses of the confining layers need to be described throughout the project area as they provide the barriers that will prevent the vertical migration of mining fluids away from the ore zone. The lithology, depositional history, and petrologic characteristics of the Graneros Group and Morrison major confining units should also be described throughout the project area, because these characteristics affect the ability of these formations to provide confinement.

The geologic data for the Inyan Kara, Graneros Group, and Morrison Formation should be collected throughout the field and with accepted industry methods. In addition to well logs, solid cores should be collected, and samples should be analyzed using a variety of analytical techniques in a laboratory. This can include, but is not limited to, petrographic microscopy, x-ray diffraction, and mass spectrometry. Additional experiments, such as laboratory column or batch sorption experiments, will be needed to develop an understanding of uranium mobility and interaction with the host rock and to support reactive transport modeling.

3. Background and Considerations for Hydrogeologic Criteria

A detailed understanding of site hydrogeologic parameters will allow the CSM to represent groundwater flow throughout the project life cycle and will support simulation of how injected and native fluids will flow within the Dewey-Burdock site. The reactive transport modeling needs to incorporate the hydrogeologic characteristics of the Inyan Kara and the confining zones (e.g., permeability, porosity, pressure, transmissivity, storativity) to predict fluid movement throughout the geologic system and over all phases of the project. Baseline data will inform the CSM and will support reactive transport model development and setting of initial conditions; monitoring data collected throughout operations can be used to verify the model predictions and update the model as needed.

As with geologic data, hydrogeologic data characterizing the ore formation should cover an area that sufficiently extends both laterally and vertically to support development of a model domain that can predict fluid movement in upgradient areas, within the ore bodies, and downgradient. For reference, [REF _Ref8141683 \h] in Appendix A shows the locations of water level measurements in the Dewey-Burdock project area. Sufficient detail/density of data throughout the project area is needed to describe localized heterogeneities that can affect fluid movement. Any such variability in the properties of the ore formation that may affect groundwater flow should be documented and discussed.

The Dewey-Burdock site poses some unique hydrogeologic characteristics that result from the geologic development of the roll-front deposits (i.e., a 90-degree shift from the original groundwater flow direction to current ground water flow). This affects the properties of the upgradient, ore zone, and downgradient areas, and should be addressed by representative hydrogeologic and geochemical data.

Unlike the site geologic characteristics, site groundwater flow patterns will change over time during the life cycle of the project. Current groundwater flow patterns and recharge areas need to be properly represented in the CSM. During the extraction phase of the project, groundwater flow will be altered as fluids are injected and withdrawn. After extraction has been completed, restoration is conducted. However, wellfields will come on-line and be closed sequentially, making the site hydrogeology dynamic. Once all restoration has been completed, the original groundwater flow regime will be allowed to

reestablish itself. Therefore, data need to characterize baseline ground water flow, inward flow during ISR and restoration (i.e., due to five-spot injection patterns and 1% bleed off), and reestablishment of the original groundwater flow regime after restoration. These data should be used to update the CSM as needed. Pressure measurements, potentiometric data, and groundwater flow data collected as baseline data and throughout the ISR life cycle will be used to validate the reactive transport model and confirm that the site is behaving as predicted.

Furthermore, ISR activities need to be monitored for their impact on shallow or near-surface aquifer behavior. Baseline groundwater surface recharge in the project area must be described and monitored for evidence of hydraulic connections with the Inyan Kara. All wells or other artificial penetrations into the Inyan Kara Group need to be considered and adequately plugged or maintained, as these can affect the pressure gradient within the formations, as well as the direction of groundwater flow.

Data should be collected using accepted industry methods and in a manner that will ensure accurate and reliable results. Whole cores should be analyzed for porosity and permeability (horizontal and vertical) by routine core analysis methods. In selecting samples for laboratory analysis, close attention should be paid to the quality of the sample because the sample's collection method can influence its measured porosity. Core samples should be clean and free of cracks or physical defects. Owners or operators should also note any possible issues with sample quality when reporting results.

Field-based hydrogeologic data can include:

- Porosity and lithology from well logging;
- Hydraulic conductivity, storativity, and transmissivity from aquifer testing;
- Potentiometric data;
- Downhole pressure data; and
- Any other tests or field-based observations relevant to the hydrogeologic regime.

Selections of data analysis methods and uncertainties in the data and methods should be discussed and acknowledged in the CSM.

4. Background and Considerations for Criteria Related to Geochemical Characteristics and Processes

Characterization of the geochemistry of the native groundwater, lixiviant, and solids within the injection layer is crucial to predict and then validate predictions of geochemical changes as ISR proceeds and as the system stabilizes after restoration. The CSM should therefore include sufficient baseline data and sampling during the project lifecycle to support simulation of the speciation and mobility of uranium and other metals. Ultimately, the reactive transport modeling that the CSM will support needs to represent how ISR operations will alter site geochemistry and the potential for off-site excursions and post-restoration rebound.

The CSM should include anticipated geochemical processes during ISR extraction (i.e., interactions between the lixiviant and groundwater and ore zone solids); during remediation (i.e., interactions between post-ISR solids and the restoration fluid); and post-restoration (i.e., between ground water and solids in the ore zone and downgradient).

The strength of the CSM will depend on having data for a sufficient number of groundwater and solids samples from throughout the site (i.e., within the injection layer, the confining zones, and upgradient, and downgradient of the site) to account for all chemical and physical characteristics of the injectate and native fluids. Existing field data, supplemented by an appropriate number of additional baseline samples for an appropriate set of chemical and mineralogic parameters, will ensure a robust model.

Monitoring will validate the model and detect excursions. Therefore, planned monitoring during the extraction, restoration, and post-restoration phases should:

- Target sampling locations that will support comparisons to modeled predictions,
- Allow for verification of the model,
- Support refinements to the CSM and reactive transport model if needed, and
- Detect excursions or contaminant rebound.

The subsections below discuss the groundwater and solid phase geochemical data that are needed and suggested methods of data collection. Section 4.3 on geochemical processes describes key interactions between the groundwater and solids as well as laboratory experiments needed for the development of a robust model.

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4.1. Groundwater Geochemistry

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4.1.1. Site-specific information

Sampling and analysis of groundwater quality in and around the Dewey-Burdock site was completed by Powertech, Inc. in 2007 and 2008 as part of underground injection permitting (Powertech, 2011) and by USGS in 2011 (Johnson 2012). In each study, monitoring wells were located within, upgradient, and downgradient of the Dewey and Burdock uranium ore zones (see [REF _Ref7769829 \h] for a map of these areas). Samples were collected from both formations containing uranium deposits (the Fall River Formation of the Inyan Kara Group, the Chilson Member of the Inyan Kara Group), overlying alluvial aquifers, and the underlying Unkpapa Sandstone. Monitoring frequencies varied by well in the

Powertech study and included monthly sampling (19 wells), quarterly sampling (14 wells), and single sample testing (12 wells). In the USGS study, one sample was collected from each of the 28 wells included in the study. Overall, the Powertech and USGS monitoring data provide good horizontal and vertical coverage of the Dewey-Burdock area. For reference, [REF _Ref8141771 \h] (see Appendix A) shows the numbers of monitoring wells by section included in the operational monitoring program planned for the project site, and [REF _Ref8141847 \h] in Appendix A shows the locations of wells where water quality data have been collected.

Samples collected by Powertech were analyzed for approximately 115 parameters, including radionuclides, metals (including uranium), major ions, and field parameters (pH, conductivity, and Total Dissolved Solids (TDS)). The USGS study analyzed approximately 75 parameters that align with the Powertech parameter set but also included the collection of isotopic measurements of hydrogen, oxygen, sulfur, and uranium to better understand the hydrogeologic system. The Powertech parameter set includes all of the baseline parameters that are required for post-restoration monitoring and compliance by the draft UIC Class III Area Permit for the Dewey-Burdock site (EPA, 2017). Most of these baseline parameters were also sampled in the USGS study (exceptions include TDS, bicarbonate alkalinity, carbonate alkalinity, nitrate, silica, mercury, thorium, and radiological parameters).

[REF _Ref8069458 \h] displays a subset of results from monitoring completed by Powertech. The table shows the range of average concentrations for wells in the Fall River and Chilson zones. Ion chemistry in both zones is characterized by relatively high concentrations of sulfate, sodium, and calcium. Predominant metals include iron, manganese, and strontium. Metals are generally found in higher concentrations within Chilson zone wells and lower in Fall River wells. Uranium concentrations are low in both zones, with a mean concentration of 0.11 mg/L reported for one Fall River well; the remaining well mean concentrations were less than or equal to 0.02 mg/L. Radionuclide levels also tend to be higher in Chilson groundwater relative to Fall River. For example, radium 226 concentrations average from less than 0.2 to 15.2 pCi/L in Fall River wells and 1.1 to 120 pCi/L in Chilson wells.

Forty-three of the parameters in the Powertech and USGS datasets have primary or secondary standards for drinking water ([REF _Ref7779520 \h]). The Powertech monitoring results show that several Fall River and Chilson samples exceed standards for sulfate, iron, manganese, uranium, gross alpha, arsenic, radium 226, and TDS. In general, exceedances occur across wells located within, upgradient, and downgradient of the extraction zones. An exception is uranium exceedances, which are limited to upgradient and downgradient wells (no exceedances were observed in the extraction zone). Similar results are evident in the USGS study, with exceedances of iron, manganese, sulfate, and thallium occurring in Fall River and Chilson wells located within, upgradient, and downgradient of extraction zones and uranium exceedances occurring in one downgradient Fall River well.

Exceedances in alluvial samples align with Fall River and Chilson results. In the alluvial samples, primary or secondary drinking water standards are exceeded for chloride, sulfate, iron, manganese, uranium, arsenic, gross alpha, and TDS. Uranium levels in the alluvial aquifer are more consistently elevated relative to Fall River and Chilson concentrations. In the Unkpapa sandstone, exceedances of drinking water standards were less common but found for pH, sulfate, iron, gross alpha, and TDS.

Table [SEQ Table * ARABIC]. Selected water quality data from the Dewey-Burdock Project Class III Underground Injection Control Permit Application (Powertech, 2013) as compared with federal primary and secondary drinking water standards (EPA, 2018).

Parameter	Federal Primary Drinking Water Standards	Secondary Standard	Fall River		Chilson	
			Minimum of Well Means	Maximum of Well Means	Minimum of Well Means	Maximum of Well Means
Field Parameters						
Field Dissolved Oxygen (mg/L)	-	-	0.07	5.42	0.14	3.29
Field pH		6.5-8.5	6.73	8.44	6.92	8.31
Major Ions						
Alkalinity, Total as CaCO ₃ (mg/L)	-	-	117.17	196.67	71	261
Calcium, Dissolved (mg/L)	-	-	30.1	368	34.74	385.5
Chloride (mg/L)	-	250	9.5	47	5	17.5
Sodium, Dissolved (mg/L)			86.6	502.5	47.42	283
Sulfate, Total (mg/L)	-	250	425.38	1442.5	388.77	1509.17
Metals						
Arsenic, Total (mg/L)	0.01	-	0.00075	0.00379	0.001	0.02
Iron, Total (mg/L)	-	0.3	0.04167	4.76417	0.08	15.3
Manganese, Total (mg/L)	-	0.05	0.03	2.485	0.04	1.74
Selenium, Total (mg/L)	0.05	-	<0.001	0.001	<0.001	0.0019
Strontium, Total (mg/L)	-	-	0.65	6.2	0.7	7.45
Uranium, Total (mg/L)	0.03	-	<0.0003	0.11	<0.0003	0.02
Radionuclides						
Radium 226, Total (pCi/L)	5	-	<0.2	15.2	1.1	120

Table [SEQ Table * ARABIC]. Parameters sampled by Powertech (2011) and USGS (Johnson, 2012) with primary or secondary standards for drinking water (EPA, 2018).

Analyte	Units	Federal Primary Drinking Water Standard	Secondary Standard
Field Parameters			
Field pH	s.u.		6.5-8.5
pH, Laboratory	s.u.		6.5-8.5
Solids, Total Dissolved TDS @ 180 C	mg/L		500
Major Ions			
Chloride	mg/L		250
Fluoride	mg/L	4	2
Nitrogen, Nitrate as N	mg/L	10	
Nitrogen, Nitrite as N	mg/L	1	
Sulfate, Total	mg/L		250
Metals, Dissolved			
Aluminum, Dissolved	mg/L		0.05-0.2
Arsenic, Dissolved	mg/L	0.01	
Barium, Dissolved	mg/L	2	

Analyte	Units	Federal Primary Drinking Water Standard	Secondary Standard
Cadmium, Dissolved	mg/L	0.005	
Chromium, Dissolved	mg/L	0.1	
Copper, Dissolved	mg/L		1
Iron, Dissolved	mg/L		0.3
Manganese, Dissolved	mg/L		0.05
Mercury, Dissolved	mg/L	0.002	
Selenium, Dissolved	mg/L	0.05	
Silver, Dissolved	mg/L		0.1
Uranium, Dissolved	mg/L	0.03	
Zinc, Dissolved	mg/L		5
Metals, Dissolved, Speciated			
Uranium, Suspended	mg/L	0.03	
Metals, Total			
Antimony, Total	mg/L	0.006	
Arsenic, Total	mg/L	0.01	
Barium, Total	mg/L	2	
Beryllium, Total	mg/L	0.004	
Cadmium, Total	mg/L	0.005	
Chromium, Total	mg/L	0.1	
Copper, Total	mg/L		1
Iron, Total	mg/L		0.3
Manganese, Total	mg/L		0.05
Mercury, Total	mg/L	0.002	
Mercury, Total A3112B	mg/L	0.002	
Selenium, Total	mg/L	0.05	
Silver, Total	mg/L		0.1
Thallium, Total	mg/L	0.002	
Uranium, Total	mg/L	0.03	
Zinc, Total	mg/L		5
Radionuclides, Dissolved			
Gross Alpha, Dissolved	pCi/L	15	
Radium 226, Dissolved	pCi/L	5	
Radium 226, Dissolved E901.1	pCi/L	5	
Radionuclides, Suspended			
Radium 226, Suspended	pCi/L	5	
Radionuclides, Total			
Radium 226, Total	pCi/L	5	

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Figure [SEQ Figure * ARABIC]. Map of areas defined as near, upgradient, and downgradient of the uranium ore zone of the Dewey-Burdock site. Reprinted from Figure 17.5 in Powertech (2013). (Permission not yet obtained.)

4.1.2. Considerations for data collection

The collection of water quality monitoring data before, during, and after ISR operations is a critical component of protecting human and environmental health and safety. Monitoring conducted prior to lixiviant injection into the ore zone (pre-ISR monitoring) provides a record of baseline conditions in the injection interval and surrounding aquifers. Data are also needed during injection, recovery, and restoration, since monitoring results can signal excursions of mining solutions, by-products, or native groundwater outside of the injection interval. In the post-restoration phase, monitoring results can be used to demonstrate compliance with post-restoration permit limits that are derived from baseline monitoring.

Throughout the life cycle of the project, ongoing data collection will allow for updates and refinement to the CSM and geochemical models that are used to evaluate potential excursions beyond the injection interval and aquifer exemption area, rebound release and transport of uranium after restoration, and release of other heavy metals into groundwater. Studies of monitoring data from other uranium ISR sites in the U.S. have documented large differences between average baseline and post-restoration concentrations of uranium, radium 226, sulfate, chloride, and metals including arsenic, iron, selenium, molybdenum, vanadium, and manganese (Saunders et al., 2016). For example, in the four studies included in a review by Saunders et al. (2016), post-restoration uranium concentrations ranged from 10 to 106 times baseline concentrations. Such findings underscore the importance of a robust CSM and geochemical modeling for evaluating potential water quality issues and guiding injection, recovery, and restoration operations.

Because uranium is mobilized during ISR operations, sampling and analysis of uranium concentrations is essential for a water quality monitoring plan. Monitoring of additional parameters further characterizes groundwater quality and provides warning signs of excursions or other water quality threats. The draft UIC Class III Area Permit for the Dewey-Burdock site (EPA, 2017) calls for the collection of 45 baseline parameters as part of the water quality monitoring program ([REF _Ref7767500 \h]). All of the baseline parameters were previously sampled by Powertech, Inc. as part of the permit application (Powertech, 2011). As mentioned earlier, many of the baseline parameters were also sampled by USGS in 2011 (Johnson, 2012); exceptions include TDS, bicarbonate alkalinity, carbonate alkalinity, nitrate, silica, mercury, thorium, and all radiological parameters. Additional parameters that should be considered for measurement include dissolved oxygen (DO), temperature, and dissolved and total organic carbon (DOC and TOC).

Table [SEQ Table * ARABIC]. Baseline parameters for groundwater quality monitoring and post-restoration compliance in the draft UIC Class III Area Permit for the Dewey-Burdock site (EPA, 2017).

Parameter	Units	Analytical Method
Physical Properties		
pH	pH Units	A4500-H B
Total Dissolved Solids (TDS)	mg/L	A2540C
Specific Conductance	µmhos/cm	A2510B or E120.1
Common Elements and Ions		
Total alkalinity (as Ca CO ₃)	mg/L	A2320B
Bicarbonate Alkalinity (as Ca CO ₃)	mg/L	A2320B (as HCO ₃)
Calcium, Ca	mg/L	E200.7

Parameter	Units	Analytical Method
Carbonate Alkalinity (as Ca CO ₃)	mg/L	A2320B
Chloride, Cl	mg/L	A4500-Cl B; E300.0
Magnesium, Mg	mg/L	E200.7
Nitrate, NO ₃ (as Nitrogen)	mg/L	E300.0
Potassium, K	mg/L	E200.7
Silica, Si	mg/L	E200.7
Sodium, Na	mg/L	E200.7
Sulfate, SO ₄	mg/L	A4500-SO ₄ E; E300.0
Total Metals		
Aluminum, Al	mg/L	E200.7, E200.8, E200.9
Antimony, Sb	mg/L	E200.8, E200.9
Arsenic, As	mg/L	E200.8
Barium, Ba	mg/L	E200.8
Beryllium, Be	mg/L	E200.7, E200.8, E200.9
Boron, B	mg/L	E200.7
Cadmium, Cd	mg/L	E200.8
Chromium, Cr	mg/L	E200.8
Copper, Cu	mg/L	E200.8
Fluoride, F	mg/L	E300.0
Iron, Fe	mg/L	E200.7
Lead, Pb	mg/L	E200.8
Manganese, Mn	mg/L	E200.8
Mercury, Hg	mg/L	E200.8
Molybdenum, Mo	mg/L	E200.8
Nickel, Ni	mg/L	E200.8
Selenium, Se	mg/L	E200.8
Silver, Ag	mg/L	E200.8, A3114 B
Strontium, Sr	mg/L	E272.1, E272.2, E200.7
Thallium, Tl	mg/L	E200.8, E200.9
Thorium, Th	mg/L	E200.8
Uranium, U	mg/L	E200.7, E200.8
Vanadium, V	mg/L	E200.7, E200.8
Zinc, Zn	mg/L	E200.8
Radiological Parameters		
Gross Alpha	pCi/L	E900.0
Gross Beta	pCi/L	E900.0
Gross Gamma	pCi/L	E901.1
Lead 210	pCi/L	E905.0 Mod.
Polonium 210	pCi/L	RMO-3008
Radium, Ra-226	pCi/L	E903.0
Thorium 230	pCi/L	EPA 910, ATSM D3972-90M

Data for the CSM and geochemical modeling need to represent the full extent of the project site, including upgradient, ore zone, and downgradient areas. The draft UIC Class III Area Permit for the Dewey-Burdock site also specifies required well locations for groundwater monitoring. Well locations are distributed within, upgradient, and downgradient of the injection wellfield (see [REF_Ref7769829 \h] above for a map of these areas) in the injection interval and in overlying and underlying aquifers. The horizontal and vertical distribution of wells prescribed by the permit is necessary to adequately characterize baseline conditions throughout the region, detect excursions, and demonstrate effective

restoration of groundwater following ISR operations. Monitoring requirements include the establishment of:

- A monitoring well ring around the perimeter of the injection wellfield;
- Monitoring wells in aquifer units overlying and underlying the injection interval within the wellfield area,
- Monitoring wells surrounding possible breaches in confining zones (based on wellfield pump test results),
- An operational monitoring program with wells located within, upgradient, and downgradient of the injection zone in the alluvial aquifer, Fall River Formation of the Inyan Kara Group, the Chilson Member of the Inyan Kara Group, and the Unkpapa Sandstone. This group includes existing wells previously sampled by Powertech, Inc. (2011) and by USGS (Johnson, 2012),
- A post-restoration monitoring program with wells located downgradient and upgradient of the injection zone, and
- Monitoring of domestic wells located downgradient of the injection zone.

Monitoring characteristics such as timing, duration, and frequency of sample collection differ between the groups of wells listed above based on monitoring purpose and objectives ([REF _Ref7767997 \h]). Wells included in the pre-ISR monitoring effort to define baseline conditions will be sampled quarterly. These results will be used to define permit limits for post-restoration compliance for the parameters listed in [REF _Ref7767500 \h] and are therefore vital to the monitoring program. Quarterly sampling will continue for all wells except domestic wells during injection, recovery, and restoration. Post-restoration sampling will be completed every 6 months for downgradient and upgradient wells included in the post-restoration compliance monitoring plan. Post-restoration sampling will also be completed every 60 days for wells that are located in the wellfield and screened in overlying and underlying aquifers. More frequent sampling will occur during ISR operations for chloride, total alkalinity, and specific conductance in the injection wellfield to detect potential excursions. Any excursions identified will trigger additional sampling.

Recommendations for groundwater sampling at ISR sites are provided by EPA (2014). These include considerations for flow rate and the importance of maintaining anoxic conditions during sample handling if the downhole conditions are anoxic. An additional consideration is the potential for enhancement of metals transport by colloids (particles 1nm – 1µm in size). If metals adsorb to colloidal particles such as clays, they may migrate with the groundwater because the particles are small enough to be mobile (McCarthy and Zachara, 1989). This mechanism should be acknowledged in the CSM if groundwater samples collected with ultrafiltration indicate the presence of uranium and other metals in the colloidal size fraction.

Table [SEQ Table * ARABIC]. Summary of groundwater quality monitoring requirements in the draft UIC Class III Area Permit for the Dewey-Burdock site (EPA, 2017).

Monitoring Well Type	Location Requirements	Monitoring Frequency Requirements			
		Pre-ISR Period	ISR Period	Restoration Period	Post-Restoration Period
Wellfield Perimeter Well Ring	1) No farther than 400 feet from the outermost wellfield well. 2) Maximum spacing of either 400 feet or spacing that will ensure no greater than a 70-degree angle between adjacent perimeter monitor wells and the nearest wellfield well.	Quarterly	Quarterly	Quarterly	-
Overlying Aquifer Wells	1) Monitoring wells completed in first aquifer unit overlying the injection interval: a density of at least one monitoring well per 4 acres of well field area. 2) Monitoring wells completed in subsequent aquifer units overlying the injection interval: a density of at least one well per 8 acres of wellfield area.	Quarterly	Quarterly	Quarterly	60 Day
Underlying Aquifer Wells	A density of one well per 4 acres of wellfield area except for aquifers below the Morrison Formation lower confining zone.	Quarterly	Quarterly	Quarterly	60 Day
Wells Surrounding Possible Breaches in Confining Zones	Based on wellfield pump test results indicating a possible breach in a confining unit.	Quarterly	Quarterly	Quarterly	60 Day
Post-Restoration Wells	Downgradient of the wellfield perimeter monitoring well ring. Minimum of three wells also located upgradient of the wellfield perimeter. Detailed location requirements are described in Appendix B of the Underground Injection Control Class III permit (EPA 2017).	Quarterly	Quarterly	Quarterly	6 Month
Operational Monitoring Wells	11 wells in alluvium located upgradient and downgradient of ore zone 9 wells in Fall River located within, upgradient, and downgradient of ore zone	-	Quarterly	-	-

Monitoring Well Type	Location Requirements	Monitoring Frequency Requirements			
		Pre-ISR Period	ISR Period	Restoration Period	Post-Restoration Period
	8 wells in Chilson located within, upgradient, and downgradient of ore zone 3 wells in Unkpapa located within and upgradient of ore zone				
Domestic Wells	Downgradient domestic wells within the Area of Review	-	Annually	-	-

4.2. Solid Phase Geochemistry and Mineralogy

This section provides context for the solid-phase geochemical criteria in the CSM criteria document. Information on solid-phase geochemistry is needed in the CSM to provide the basis for understanding interactions between the fluids (groundwater, lixiviant, and restoration fluid) and aquifer solids during the stages of the ISR project (including post-restoration) and in the different parts of the project area (i.e., upgradient, ore zone, downgradient). Information on geochemical processes is presented later in this document.

To develop a CSM that represents the project site as realistically as possible, quality geochemical data from core samples are needed that are representative of the project site and that have been analyzed with the appropriate methods. This section describes typical minerals found in uranium roll-front deposits, methods for analysis of aquifer solids, and basic information about mineralogy at the Dewey-Burdock site. Requirements for solids sampling in the draft Class III area permit for Dewey-Burdock site (EPA, 2017) are also included.

[REF_Ref7947992 \h] presents minerals reported in roll-front deposits in the U.S. These include the principal uranium ore-bearing minerals (uraninite, pitchblende, and coffinite) as well as those containing other metals of concern (vanadium, molybdenum). The iron-bearing minerals are significant for several reasons:

- Iron is redox-sensitive and will change form as redox conditions change;
- Other metals, such as arsenic, may be co-precipitated with iron-bearing minerals such as pyrite; and
- Minerals with oxidized iron Fe(III) can adsorb uranium and other metals from solution (see Section 4.3.3).

Notably, the U(IV) ore minerals (uraninite, pitchblende, coffinite) have low solubilities, keeping uranium (as U(IV)) in reduced sediments and immobilized.

Table [SEQ Table * ARABIC]. Minerals reported in uranium roll-front deposits in the U.S. (Source: Saunders et al., 2016).

Mineral	Formula	Mineral	Formula
Uraninite	UO ₂ (crystalline)	Jordesite	MoS ₂ (amorphous)
Pitchblende	UO ₂ (amorphous)	Haggite	V ₂ O ₂ (OH) ₃

Mineral	Formula	Mineral	Formula
Coffinite	$U(SiO_4)_{0.9}(OH)_{0.4}$	Paramontroseite	VO_2
Carnotite	$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$	Montroseite	$(V^{3+}, Fe^{3+})O(OH)$
Native selenium	Se	Hematite	Fe_2O_3
Native sulfur	S	Goethite	$FeOOH$
Ferroselite	$FeSe_2$	Siderite	$FeCO_3$
Pyrite	FeS_2	Gypsum	$CaSO_4 \cdot 2H_2O$
Marcasite	FeS_2	Calcite	$CaCO_3$
Mackinawite	FeS	Kaolinite	$Al_2Si_2O_5(OH)_4$
Molybdenite	MoS_2 (crystalline)	Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

In a typical roll-front deposit setting, the minerals in the sandstone aquifer solids upgradient of the ore zone have been oxidized over geologic time by groundwater from the recharge area. Iron in these sediments occurs as hematite and possibly magnetite, although the magnetite may be oxidized to hematite. Uranium-bearing minerals are not expected in this zone because uranium is mobile under oxidizing conditions and will have been dissolved and transported downgradient. In the alteration zone between the oxidized upgradient sandstone and the ore zone, siderite, goethite, and ferroselite may be found. In the ore zone, the sediments reflect reducing conditions and can include uraninite, coffinite, pyrite, selenium, and ilmenite. Downgradient of the ore zone, the sediments also reflect reducing conditions and can contain pyrite and organic matter. [REF _Ref7854310 \h] is a generalized depiction of mineralogical zonation in a roll-front deposit. Exact mineralogy and geochemistry can vary among deposits, and the pattern of downgradient redox zonation at the time of ore formation may change if groundwater flow changes over geologic time.

Figure removed pending permission from authors

Figure [SEQ Figure * ARABIC]. Mineral zonation in a typical uranium roll-front sandstone deposit. Source: Powertech (2013), Figure 17.2. (Permission not yet obtained.)

Several methods can be used for basic characterization of aquifer solids ([REF _Ref8148741 \h]). Petrographic analysis with polarized light microscopy is a standard step to identify mineralogy and relationships among minerals. Additional methods provide further information on mineralogy and textures (e.g., mineral overgrowths vs. discrete grains) and the chemical composition of individual minerals or whole samples. Additional parameters for solid-phase characterization are suggested by EPA's draft considerations for ISR post-monitoring (EPA, 2014). These include ion exchange capacity, extractable sulfide, sorption capacity, adsorbed uranium, microbial population, and other parameters that may be useful for evaluating geochemical processes at an ISR site. In particular, it is important to know the forms in which uranium occurs in the aquifer solids (in minerals, adsorbed to the surfaces of other minerals, associated with organic matter). For data for the CSM, selected solids characterization methods and the information sought should be explained, and any uncertainties or limitations acknowledged.

Table [SEQ Table * ARABIC]. Methods for analysis of aquifer solids

Method	Purpose	Notes
Polarized light microscopy	Petrologic analysis, mineral identification, mineral textures (e.g., overgrowths, discrete grains)	Initial baseline step in analyzing rocks and sediments. Does not provide chemical analysis other than knowledge of the general chemical formulas of minerals. Cannot confirm sulfide minerals.
X-ray diffraction	Mineral identification based on mineral structures	Cannot detect poorly crystalline or amorphous solids. Trace constituents such as uranium minerals will be present in too small an amount to be detected. Does not provide chemical analysis or relationships among minerals.
Scanning electron microscopy (SEM) or electron microprobe with SEM capabilities	Petrologic analysis, mineral identification, mineral textures, chemical analyses of minerals	Complement to polarized light microscopy. Imaging can be used to identify minerals and relationships among minerals. Individual mineral grains can be analyzed chemically either qualitatively or quantitatively.
X-ray absorption near edge structure (XANES)	Oxidation state of uranium	
Acid digestion for elemental analysis	Whole-rock chemical analysis	Elements quantified by inductively coupled plasma–mass spectroscopy. Also measures $^{234}\text{U}/^{238}\text{U}$ activity ratios.
Method ASTM D 5373	Organic carbon analysis	CHN elemental analyzer

A variety of chemical methods have been used to quantify the different forms of metals in sediments and soils via sequential extractions. In sequential extractions, a series of chemical extractants is used, with each targeted to a particular fraction of the metals pool (e.g., poorly crystalline, crystalline, organically bound, adsorbed) (e.g., Heron et al., 1994; Ryan and Gschwend, 1991). After the sediments are extracted and then filtered out, the liquid is analyzed for the elements of interest. Because the chemicals used to extract the different forms of the metals are not perfectly selective, the results can be considered “operational.” They are, however, useful for an analysis of metals speciation and temporal and spatial trends in the geochemistry of the solids. Sequential extractions are valuable because the different forms of metals have different mobilities. For iron and manganese, the oxidized forms serve as substrates to adsorb metals, so their forms have implications for how effectively uranium and other metals will be retained.

4.2.

4.3.

4.2.1 Site-specific information

At the Dewey-Burdock site, the reduced sandstones are described as containing organic material, small crystals of pyrite with trace amounts of transition metals (Cu, Ni, Zn, Mo, and Se), and minor minerals including ilmenite, apatite, zircon, and tourmaline (Powertech, 2013; Chapter 18). In the oxidized zone, iron is present in the form of iron oxides (hematite, goethite), coatings on other minerals, and as

separate grains or pseudomorphs after pyrite. Clay minerals are present, and there is no organic matter. Trace amounts of uranium originally present at the time of deposition would have been mobilized during oxidation and migrated downgradient. In the ore zone, the sandstone contains the uranium minerals uraninite and coffinite; these are described as occurring both as crystals within the sandstone (interstitially) as well as coatings on the sand grains and intergrown with pyrite and montroseite (a vanadium mineral). Other vanadium minerals (haggite and doloresite) are found in this zone as well as the molybdenum mineral jordisite on the originally downgradient side of the ore zone. Native arsenic and selenium are found on the originally upgradient side of the ore zone. Calcite and pyrite were also formed during ore formation.

Although the sediments downgradient of the ore zone at a roll-front deposit generally reflect reducing conditions, there has been a 90-degree shift in groundwater flow direction at the Dewey-Burdock site. Groundwater flow at the time of ore formation was from the northwest to the southeast; current-day flow is from the northeast to the southwest. Because of this, there are oxidized sediments downgradient of the ore bodies rather than reduced sediments; reduced sediments are shown further downgradient of the ore bodies in [REF _Ref8143583 \h].

Figure removed pending permission from authors

Figure [SEQ Figure * ARABIC]. Redox zone map of the Dewey-Burdock project area, showing the project area, the direction of groundwater flow at the time of ore formation, and the current groundwater flow direction. Source: Johnson and Tutu (2015). (Permission not obtained.)

Data from Johnson et al. (2013) show differences in uranium concentrations between the reduced, oxidized, and ore zones. In reduced sediments of the Lower Chilson, uranium concentrations in the aquifer solids range from 4-96 ppm. In the ore zone (also reduced), concentrations ranged from 9.04 ppm in the upper ore limb to 606 ppm within the ore zone. In the oxidized zone, uranium concentrations are only 1.2-2.7 ppm. In the Fall River formation, reduced solids had 4.16 to 9,810 ppm of uranium; oxidized sediments are lower, with a minimum of 0.868 ppm and a high of 68.1 ppm. Johnson et al. (2013) also note high vanadium concentrations in the ore samples. In particular, three Fall River samples with high radioactivity had vanadium concentrations of 180, 400, and 38,600 ppm. For reference, [REF _Ref8142020 \h] (in Appendix A) shows the locations of cores and the numbers of samples for each core for which complete solids phase characterization data were available as part of the USGS research at the Dewey-Burdock site.

USGS research (Johnson et al., 2013) has also shown differences in the solid-phase geochemistry between the Dewey and Burdock areas based on 31 core locations. In the Dewey area (Fall River formation), the aquifer solids have a higher calcite content, no organic carbon, and evidence that uranium has been dissolved. The uranium ore samples also have high vanadium content. In the Burdock area, the calcite content is lower, there is more organic carbon, and vanadium content is lower. Uranium was found to be associated with organic matter. These differences mean that the two areas may differ in the geochemical processes governing the mobility of uranium between the two areas.

Although the goal of ISR is to oxidize and dissolve uranium minerals to mobilize and recover the uranium, uranium can remain in the aquifer solids after ISR. At an ISR site in Wyoming (Smith Ranch-Highlands), researchers documented both oxidized (U(VI)) and reduced (U(IV)) uranium in the post-

restoration ore zone, with a great deal of variability among samples (concentrations ranged from 5 to 1,920 ppm among the core intervals). Reduced uranium was found to be associated with organic matter (possibly as the minerals uraninite or coffinite) in intergranular spaces. Oxidized uranium was either adsorbed to iron oxides or occurs as newly precipitated mineral coatings (Gallegos et al., 2015). These remaining phases will vary in how readily they will be mobilized, and the more labile fractions can serve as a source of uranium in the groundwater.

4

4.2.1

4.2.2 Considerations for data collection

Differences in characteristics between the reduced and oxidized aquifer solids, the variability among samples, and the potential for residual uranium to remain in the solids after restoration underscore the importance of having adequate spatial and temporal coverage for samples at the site: upgradient, within the ore zones, and downgradient as well as before ISR, after ISR, and after restoration. After restoration, solids in the ore zone should be recharacterized to evaluate whether there have been changes in mineralogy and textures and to quantify changes in bulk chemistry.

When sampling reduced sediments, it is important to maintain these conditions through sample handling, storage, and analysis. If reduced sediments are exposed to air, the oxidation state of iron, manganese, and other redox-sensitive elements may change, including the oxidation state and mobility of uranium. Such samples need to be retrieved from cores in a manner that avoids exposure to air. Samples should be sealed in airtight containers and kept on ice or frozen in the field. In the laboratory, sample handling should be done in a glove box or another method that minimizes exposure to air.

The draft Class III area permit for Dewey-Burdock (EPA, 2017) provides the following requirements for core sample collection.

Injection Zone Core Sample Collection from Monitoring Wells Located Down-gradient of Wellfields

- a. The Permittee shall collect a minimum of two (2) cores per wellfield through the proposed injection interval while drilling the down-gradient perimeter monitoring wells ring wells or the Down-gradient Compliance Boundary Wells.
- b. Core shall be recovered and preserved in a manner to prevent further oxidation so as to be representative of in-situ geochemical conditions for use in columns tests as part of Post-Restoration Monitoring to verify that no ISR contaminants will cross the down-gradient aquifer exemption boundary.

4.3. Geochemical Processes

A complex interplay of geochemical processes governs interactions between groundwater and aquifer solids. These interactions dictate the mobilization and immobilization of uranium and other heavy metals such as vanadium, arsenic, and molybdenum. Furthermore, changes in the groundwater

chemistry in the restored zone will affect the downgradient zone. For a realistic CSM and geochemical model of the Dewey-Burdock site, the CSM needs to include the appropriate geochemical processes.

Below are general descriptions of some of the relevant geochemical processes; the reader is encouraged to refer to additional sources for more details on the geochemistry of ISR sites. This section also provides discussion on laboratory and field-scale experiments needed to support the development of the CSM and the geochemical modeling.

4.3.1. Redox geochemistry of uranium

Uranium occurs in nature in two oxidation states, U(IV) and U(VI). U(IV) is immobile as it occurs in U(IV)-bearing minerals (e.g., uraninite, coffinite; see [REF _Ref7947992 \h]) with low solubilities. The oxidized form is more mobile than the reduced form at the pH and redox conditions commonly found in groundwater systems. Therefore, processes that affect the redox state in the subsurface, both over geologic time and during ISR, affect the redox state of uranium and other redox-sensitive metals, the forms of the metals (mineral, dissolved, adsorbed onto other minerals), and their ability to move with groundwater. Currently, the groundwater at the Dewey-Burdock site is low in oxygen, and uranium concentrations in groundwater are low. Vanadium also commonly occurs in uranium deposits ; it is redox-sensitive and like uranium, is more soluble under oxidizing conditions than reducing conditions (Hem, 1989).

The predominant forms (species) of U(VI) in groundwater are shown by geochemical speciation modeling to be uranyl-carbonate complexes and calcium-carbonate-uranyl complexes (Dong & Brooks, 2006; Saunders et al. (2016)). Predominant species in groundwater as shown by speciation modeling include: UO_2CO_3^0 , $(\text{UO}_2)\text{CO}_3(\text{OH})_3^-$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$.

The Eh-pH diagram below ([REF _Ref8143609 \h]) illustrates the general stabilities of uranium in groundwater as a function of pH and redox status (pE) in a closed system. For example, in reducing conditions (pE below zero), the most stable form is the mineral uraninite (UO_2). Under oxidizing conditions (pE above zero) and a pH between about 6 and 8, uranium will be in the oxidized state and will form dissolved complexes with carbonate. An Eh-pH diagram varies according to which constituents are represented. For example, this diagram is not specific to the Dewey-Burdock site (e.g., does not include calcium complexes and will not). However, it is a useful example to show generally how the predominant form of uranium can change with changes in the pH and redox status.

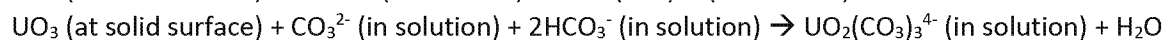
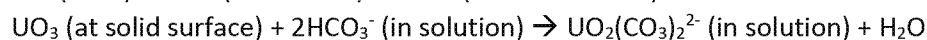
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Figure [SEQ Figure * ARABIC]. Diagram for uranium for a closed system showing stabilities of uranium species as a function of pH and redox status (represented by pe) (total U concentration: is 10^{-6} M and total dissolved CO_2 and H_4SiO_4 concentrations: 10^{-3} M) (Source: Ruiz et al., 2016; diagram prepared by Thomson after Langmuir, 1997) (permission not obtained)

4.3.2. Oxidative dissolution and complexation during ISR

During ISR, the oxygen in the oxygen/bicarbonate lixiviant proposed for this project will oxidize the ore minerals (uraninite and coffinite). The oxidation state of uranium will increase to U(VI), and the bicarbonate will promote the formation of soluble uranium carbonate complexes(Johnson et al., 2013).

The equations below describe the oxidative dissolution of uraninite by the oxygen and the formation of a dissolved uranium carbonate complex.



In the presence of calcium in the groundwater, dissolved ternary calcium-uranyl-carbonate complexes will form, such as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (Dong and Brooks, 2006).

4.3.3. Sorption

Adsorption and desorption will be important in controlling migration of uranium within the ore zone and in the oxidized sediments downgradient of the ore zone during extraction, when uranium is mobilized, during restoration, and potentially post-restoration in the event of rebound mobilization of uranium.

Uranium in solution as uranyl ion (UO_2^{2+}) can adsorb onto clays, iron oxyhydroxides, manganese oxyhydroxides, and sulfide minerals. Iron and manganese oxides (oxyhydroxides in particular) are highly effective at retaining metals. At the Smith Ranch-Highlands project, weathered pyrite, chlorite and iron oxide surfaces were identified as important for removal of uranium from groundwater via adsorption (Gallegos et al., 2015); such phases can therefore provide a barrier to downgradient migration of uranium.

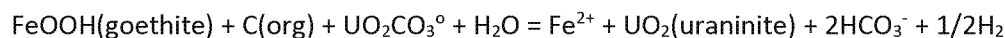
The effectiveness of adsorption as a mechanism for retaining uranium and other metals varies with geochemical conditions. Under oxidizing conditions, reduced iron- and manganese-bearing minerals would be oxidized to form secondary minerals that can adsorb uranium and other metals.

Changes in groundwater chemistry such as increased pH or increased TDS can promote desorption and mobilization of previously retained uranium, either within the ore zone or in the oxidized zone downgradient. Under changing redox conditions, iron and manganese in the solids may be reduced and dissolved (e.g., by iron-reducing bacteria), releasing metals that are adsorbed onto their surfaces or co-precipitated. Because groundwater chemistry and redox conditions at the project site will change over time, sorption of uranium and other metals in the ore zone and downgradient need to be considered when modeling post-restoration mobility of uranium.

4.3.4. Microbially mediated processes

Microorganisms can affect uranium mobility during ISR extraction (either positively or negatively) through the oxidation or reduction of uranium and other redox-sensitive elements, especially iron. These processes can be considered for inclusion in the CSM. The reduction of iron by microbial activity coupled to the degradation of organic matter under anoxic conditions is well established (e.g., Lovley et al., 1986), and U(VI) (as the uranyl ion) may also be microbially reduced (Anderson et al., 2003). Researchers have noted the possibility of using these processes to develop methods for the bioremediation of uranium (e.g., Zammit et al., 2014).

As an example, the following equations show the reduction of both iron (as minerals) and dissolved uranium, coupled to the breakdown of organic matter in the solids, to form reduced uranium minerals (Saunders et al., 2016):



Or



4.3.5. Geochemical and mineralogic factors influencing uranium mobility

Several characteristics of groundwater and aquifer solids may increase or decrease uranium mobility via the processes described above. The following are examples of significant factors that can control uranium mobility:

Calcite in aquifer solids: Equilibrium between the groundwater and calcite in the solids decreases the adsorption of uranium onto sediments due to the increased formation of uranyl carbonate complexes on account of the additional carbonate in the groundwater.

pH: Small changes in pH can have a large effect on uranium mobility due to changes in the aqueous speciation (Johnson and Tutu, 2015). At higher pH, there is increased formation of soluble calcium-uranyl carbonate complexes in solution. Consequently, there is less uranyl ion to adsorb onto mineral surfaces. However, at higher pH, calcite precipitation would be promoted, promoting less calcium and carbonate available in solution for complexation with uranium, thereby reducing uranium mobility.

Carbonate content in groundwater: Uranium is most soluble in oxidizing waters with a high carbonate content. Increased carbonate concentrations in the groundwater will promote formation of uranyl-carbonate complexes, maintaining more uranium in solution and limiting adsorption.

4.3.6. Potential for residual uranium in the restored zone

Several factors could contribute to the potential for residual uranium in the restored zone and rebound mobilization after restoration. Research at the Smith Ranch-Highlands project indicates that there can be spatial variability in the degree of oxidation in the ore zone due to variability in the contact between the solids and lixiviant as well as natural variability in the geochemical characteristics of the solids. If regions of groundwater flow get bypassed, local areas may not be effectively reached by the lixiviant. There may also be locally reducing conditions due to variability in sediment organic carbon content. Also, the iron in pyrite can chemically reduce U(VI) to the more immobile U(IV). These processes can contribute to the persistence of U(IV) in the ore zone.

As noted above, secondary iron oxides formed by oxidation during the extraction phase may adsorb U(VI) (as uranyl ion; UO_2^{2+}), helping to limit the migration of uranium. However, the U(VI) adsorbed onto iron oxide surfaces can serve as a source of mobile uranium if groundwater chemistry changes. For example, a shift in pH as upgradient water moved into the restored zone could cause a rebound of uranium in groundwater that could exceed baseline values.

If reducing conditions persist or are reestablished in the restoration zone, this would promote the immobilization of uranium. However, dissolution of iron oxides under reducing conditions would release any adsorbed uranium and other metals.

4.4. Laboratory and Field-Scale Experiments

Laboratory experimental work is needed to determine parameters for modeling the geochemical interactions between the fluids and aquifer solids. These include batch and column experiments to evaluate adsorption/desorption and dissolution/precipitation (due to leaching with lixiviant or reactions between the solids and native groundwater). Sorption parameters specific to the Dewey-Burdock site are particularly needed due to the important role sorption is expected to play in retarding uranium mobility in oxidized sediments.

Batch experiments: Batch experiments can be used to determine equilibrium parameters. To conduct a batch experiment, a sample of aquifer solid is added to a vial, and fluid is added. The fluid may represent groundwater or lixiviant, and concentrations of important constituents are varied in different vials to test their effects. The vials are agitated for a set period of time to allow the fluid and solids to reach equilibrium, and the fluid is analyzed for changes in the concentrations of constituents. The important variables for the Dewey-Burdock site that would be addressed in experiments include pH, uranium concentration, (Eh or dissolved oxygen if redox conditions are of concern in the experiment), and minerals in the solids such as calcite).

Column experiments: Column experiments involve packing a column with aquifer solids and allowing fluid to pass through from the top at a set rate using a pump; fluid samples are collected at the bottom. As with the batch experiments, fluid composition is formulated to test different chemical compositions. By passing the fluid through the column, column experiments can be used to evaluate the rates of reactions and are used for modeling transport of constituents in the fluids through the subsurface. A tracer that does not interact with the solids, such as chloride, is passed through first to determine how the fluid moves through the column.

Several studies detail batch and column experiments that are relevant to ISR projects, including data needs and recommendations for future work (Johnson et al., 2013; Deutsch et al., 1983; Ben Simon et al., 2014; Ruiz et al., 2016; Stone, 2017; Johnson et al., 2016b).

The draft area Class III permit for Dewey-Burdock (EPA, 2017) sets the following specifications for laboratory experimental work:

Laboratory Column Testing to Verify Attenuation Capability of Down-gradient Injection Zone Aquifer 1.

Once wellfield restoration has been completed in a wellfield and restored wellfield groundwater is available for use in the following laboratory tests, the Permittee shall use the injection zone core samples collected as required under Part II, Section D.5 to conduct columns tests according to the following specifications:

- a. Compile vertical composite samples from single cores and conduct at least two laboratory bench-scale column tests per wellfield on the composite samples.
- b. The two column tests shall be conducted using the following leachates:
 - i. One column test shall be conducted using unrestored wellfield groundwater taken from a wellfield in which uranium recovery has been initiated, but before groundwater restoration has begun, and

- ii. The second column test shall be conducted using restored wellfield groundwater.
- c. The column testing fluids shall be analyzed for the analytes in Table 8 before and after recovery from the column so that changes in analyzed constituent concentrations may be determined.

Additional details on the procedures, goals, and interpretation of column tests for this project are included in the fact sheet for the Dewey-Burdock Class III area permit (EPA, 2019). See also Section 3.3.5 of the Conceptual Site Model criteria document for considerations related to laboratory batch and column experiments.

Field-scale experiments: A next step beyond laboratory experiments would be scaling up to field-based experiments. By working at a scale more similar to the project, such experiments can provide data for more realistic model parameters. At least two wells are needed; one to inject the experimental fluid and one to take samples. Field-based studies are more involved logistically and can be expensive. Also, the entire volume of solids through which the fluids flow cannot be characterized. However, the effects of any local heterogeneities that cannot be captured at the laboratory-scale will be represented in field-based data.

5. Synthesis of Data into a Conceptual Site Model

Data can be synthesized to form a CSM using a variety of methods of presentation. Because the Dewey-Burdock site has detailed plans for an ISR project and the CSM will be used to support reactive transport modeling, the CSM will need to be accordingly detailed. Narrative will be needed to describe site features and the processes included in the CSM. Although there is no one standard way of preparing a CSM, graphics may include maps, cross-section or block diagrams, and flow charts. The goal of this CSM is to convey site characteristics and relevant processes (geochemical, biogeochemical, and hydrogeologic processes) and how they affect groundwater quality and potential contaminant migration during the lifecycle of the ISR project. This includes portraying factors affecting possible off-site excursions and the potential for rebound concentrations of uranium and other metals after restoration. To incorporate the CSM into the development of a reactive transport model, CSM software may be considered.

Because the formats of CSMs can vary, the following references are noted as examples from various project types. Appendix B contains examples of CSM graphics.

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Water Levels in Inyan Kara Wells: UIC Permit Application Appendix F

Monitoring Wells

Figure A- [SEQ Figure_A- * ARABIC]. Water levels in wells in the Inyan Kara. Data source: Draft UIC Class III permit application, Appendix F.

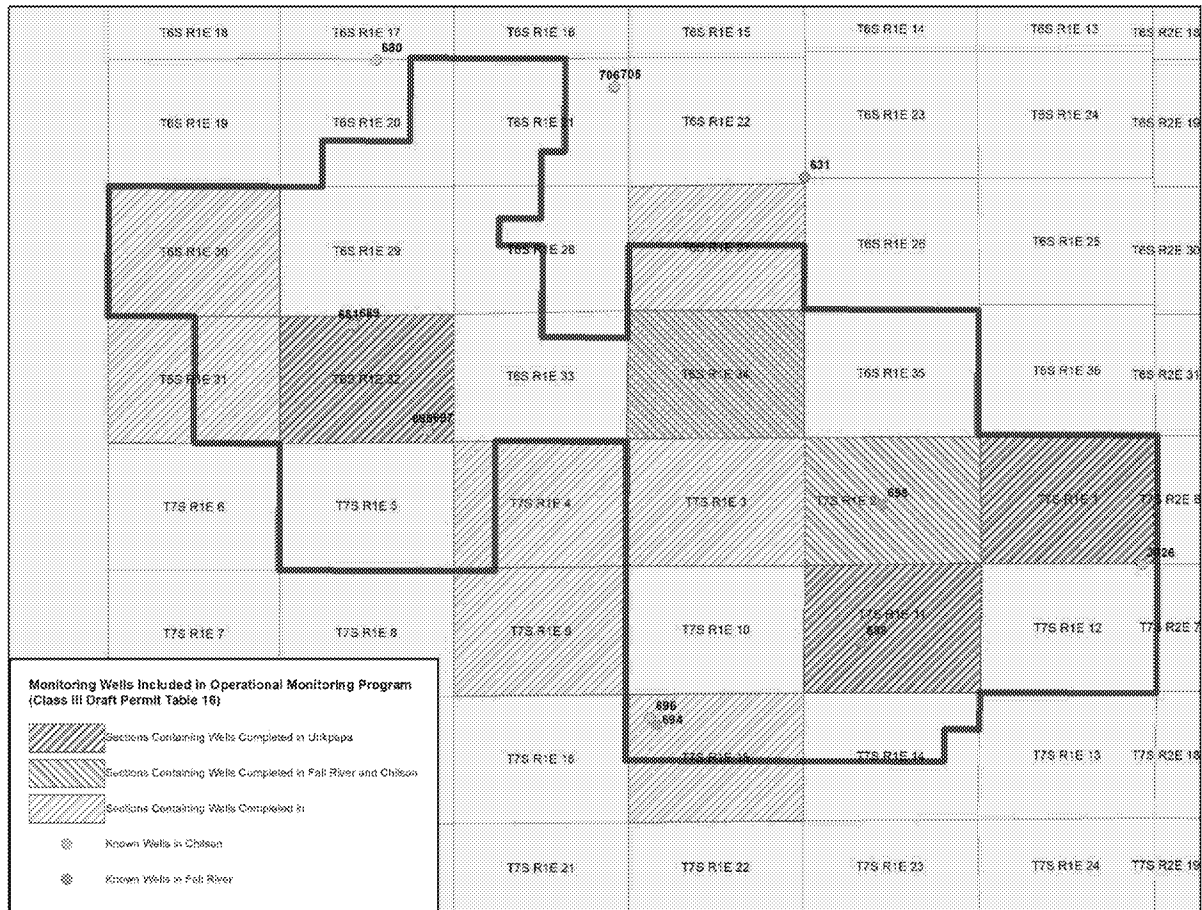


Figure A- [SEQ Figure_A- * ARABIC]. Monitoring wells included in the operational monitoring program. Data source: UIC Class III draft permit application, Table 16.

Figure removed pending permission from authors

Figure A- [SEQ Figure_A- * ARABIC]. Locations and screened intervals of water quality wells at the Dewey-Burdock project site. Data source: Johnson et al., 2012.

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Figure A- [SEQ Figure_A- * ARABIC]. Locations and numbers of samples of cores at the Dewey-Burdock site.
Data source: Johnson et al., 2013.

DRAFT

Appendix B. Example Graphics from Conceptual Site Models

Below are examples of CSM graphics showing the significant site features and processes. These examples are from various types of subsurface projects and show how cross sections, flow charts, and maps can illustrate site characteristics and relevant geochemical and hydrologic processes. [EPA: We are in the process of requesting permission for those images you would like to keep.]

Figure removed pending permission from authors

Source: Logan, M., Gillow, J., and Murphy, R. 2015. Geochemical Conceptual Site Models Validated by Speciation Data to Support In Situ Treatment Strategies for Metals. Arcadis. Retrieved from: [[HYPERLINK "https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf"](https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf)]_Accessed 5/31/2019.

This diagram shows a geochemical site conceptual model developed to help assess the potential for arsenic mobility at a site with historical mining. It shows the groundwater constituents, minerals, and processes that affect the speciation (chemical forms) and mobility of arsenic.

Figure removed pending permission from authors

Source: Logan, M., Gillow, J., and Murphy, R. 2015. Geochemical Conceptual Site Models Validated by Speciation Data to Support In Situ Treatment Strategies for Metals. Arcadis. Retrieved from: [[HYPERLINK "https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf"](https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf)]_Accessed 5/31/2019.

This figure is part of the development of a geochemical site conceptual model for a site with historical mining activities. The map shows that site characterization, including concentrations and forms of arsenic (e.g., solid phase) and groundwater flow direction.

Figure removed pending permission from authors

Source: Logan, M., Gillow, J., and Murphy, R. 2015. Geochemical Conceptual Site Models Validated by Speciation Data to Support In Situ Treatment Strategies for Metals. Arcadis. Retrieved from: [[HYPERLINK "https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf"](https://www.esaa.org/wp-content/uploads/2015/06/08-Logan.pdf)]_Accessed 5/31/2019.

This figure is part of the development of a geochemical site conceptual model for a site with historical mining activities. It illustrates the oxidizing and reducing zones along with the basic geologic setting, and it shows the basic geochemical characteristics and processes.

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Source: New Jersey Department of Environmental Protection. 2011. Site Remediation Program: Technical Guidance for Preparation and Submission of a Conceptual Site Model. Version 1.0. [

HYPERLINK "https://www.nj.gov/dep/srp/guidance/srra/csm_tech_guidance.pdf"]_Accessed 5/31/2019.

This diagram in a site conceptual model guidance document shows maps and a cross section to illustrate sampling at the site and other information.

Figure removed pending permission from authors

Source: Nikolaidis and Shen, 2000. Conceptual site model for evaluating contaminant mobility and pump-and-treat remediation. Global Nest: the Int. J. Vol 2, No 1, pp 67-76. [HYPERLINK "<https://journal.gnest.org/sites/default/files/Journal%20Papers/Nikolaidis.pdf>"]_Accessed 5/31/2019.

This flow chart shows the general development process of an augmented site conceptual model.

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Source: Zammit, C., Brugger, J., Southam, G., and Reith, R., 2014. In situ recovery of uranium — the microbial influence. Hydrometallurgy 150, 236–244.

This cross-section shows a conceptual model of the geochemical processes associated with a uranium roll-front deposit.